A New Route to Phosphonium Polymer Network Solids via Cyclotrimerization

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ABSTRACT: An organo-main group network solid having tetrahedral phosphonium vertices was prepared from a diacetyl monomer via a straightforward cyclotrimerization reaction. The network solid composition was examined by FT-IR spectroscopy and elemental microanalysis, revealing quantitative reaction of carbonyl moieties and a 67% degree of cross-linking. The reaction yielded a material having a layered structure that is comprised of an amorphous polymer and which is thermally stable up to 370 °C in air with a char yield of 40% upon heating as high as 800 °C under N_2. The polymer is stable to 6 M NaOH(*aq*) at 60 °C for 24 h and takes up only 10.63% of water by mass at room temperature. The surface morphology, as examined by AFM, revealed a very smooth as-prepared film (RMS roughness of 3 nm). The specific surface area measured by BET analysis with N_2 gas is 9 m^2 g^{-1}, indicating a type II, nonporous material. Physisorption with CO_2 revealed that the phosphonium network solid has additional affinity for CO_2, suggesting that such materials may have use for applications such as CO_2 capture. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *55*, 1620–1625

KEYWORDS: cyclotrimerization; network; phosphonium polymer

INTRODUCTION Organic network solids support an everexpanding field of research due to their broad applications in gas storage/separation[1–5] and catalysis.[6,7] Much effort has been devoted to the development of polymer scaffolds bearing diverse functional units to have precise control of physical (pore size, surface area)[8,9] and chemical properties (polar or ionic).[10] Compared with traditional organic frameworks, ionic hypercrosslinked polymers, specifically those involving ionic liquids as monomers, have attracted growing attention. These materials can possess good thermal and chemical stability, properties that can be tuned upon simple counterion exchange, and which can readily form layer-by-layer self-assembled films with other ionic polymers.[11–20] For example, Yang et al. reported an alkaline anion exchange membrane **R1** (Scheme 1) comprised of copolymerized imidazolium-functionalized ionic liquids with styrene and acrylonitrile. Membranes of **R1** demonstrated good hydroxide ion conductivity and mechanical properties suitable for use in alkaline fuel cells.[21] Furthermore, cationic polymers with phosphonium units are widely used as organocatalysts, for example, for CO_2 capture and conversion.[6]

Among ionic polymers, phosphonium polyelectrolytes exhibit outstanding chemical stability (i.e., **R2** in Scheme 1) compared with their ammonium analogs.[22] Tetraarylphosphonium salts of the form $[PAr_4]^+[NTf_2]^-$ are also thermally stable to heating for several days at 425 °C in air, making them promising candidates for ionic units in high-stability polymers.[23] Our group recently reported a new route to tetraarylphosphonium polyelectrolytes having decomposition temperatures of up to 460 °C, with one that is stable at 65 °C in 6 M NaOH(*aq*) for at least 24 h (**R3** in Scheme 1).[24] Such robust properties are necessary for their use in antibacterial coatings[25,26] and as membranes in alkaline fuel cells and related electrochemical energy conversion technologies.[27]

Despite their intriguing properties, less work has been reported involving phosphonium salts in organic frameworks compared with the vast number of papers published every year related to organic polymer networks. This is probably because of the less-explored synthetic routes for polymers with tetraarylphosphonium units and the relative difficulty of handling air-sensitive phosphorus precursors. The synthetic routes for preparing ionic organic frameworks generally employ either bifunctional charge-bearing monomers,[21,28] or post-polymerization modification of a neutral network solid to introduce ionic moieties.[22]

Additional Supporting Information may be found in the online version of this article.

A)

B)
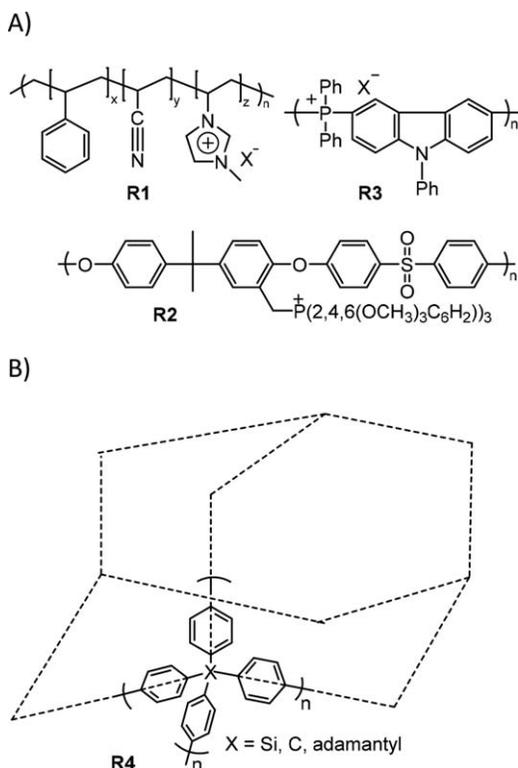
SCHEME 1 Examples of polyelectrolytes (A) and a network solid having tetrahedral vertices (B).

A facile synthetic route with fewer steps and more conveniently available monomers is desired. Among cyclotrimerization routes to porous solids, polymers in which polymerization proceeds via acid-catalyzed formation of 1,3,5-triarylbenzene units from acetophenone derivatives is one of the most-extensively studied methods.[29] Kaskel's group, for example, reported that porous monolithic organic frameworks that hold the shape of the reaction vessel can be easily prepared via cyclotrimerization of the monomers in molten *p*-toluenesulfonic acid, which serves as both the acid catalyst and solvent.[30] Other studies have examined organic networks having tetrahedral vertices, for example in **R4** (Scheme 1B).[4]

Bearing these studies in mind, we envisioned that cyclotrimerization of a diacetyl-functionalized tetraarylphosphonium salt could serve as a tetrahedral vertex upon cyclotrimerization to yield an ionic framework having excellent thermal and alkaline stability. Herein, a simple method for preparing ionic network solids containing tetraarylphosphonium units is described. The surface area, differential affinity for CO_2 and N_2, water uptake and film morphology were also examined.

EXPERIMENTAL

General Considerations

Air-sensitive reactions were performed in an MBraun UNILab glovebox under nitrogen. Chemicals were used without further purification from suppliers.

Synthesis of Bis(4-Acetylphenyl)-Diphenylphosphonium Bromide (M1)

In a 100 mL pressure vessel, diphenylphosphine (4.000 g, 21.48 mmol), 4′-bromoacetophenone (8.980 g, 45.11 mmol), diisopropylamine (2.174 g, 21.48 mmol), and $NiBr_2$ (0.282 g, 1.29 mmol) were mixed in 7 mL ethylene glycol with a magnetic stir bar. The tube was sealed with a Teflon cap equipped with a viton O-ring under N_2. The reaction was carried out under N_2 at 180 °C for 15 h. A mixture of 80 mL of acetonitrile, 30 mL of deionized H_2O, and 30 drops of HBr were added to the green crude mixture. The mixture was stirred in a 40 °C water bath and periodically checked until no resonances attributable to the ketal group were present in the ^1H NMR spectrum. Then the mixture was extracted by dichloromethane and washed with 1 M NaBr(*aq*) solution twice and deionized (DI) water once. The organic layer was collected and dried over anhydrous Na_2SO_4 overnight. All volatiles were removed under reduced pressure and the crude product was precipitated by addition of 400 mL of diethyl ether. The light yellow powder was collected by vacuum filtration and dried in a vacuum oven overnight. Chromatography was carried out over silica using acetonitrile and methanol (10:1, v/v) as the mobile phase to yield the product as a pale yellow powder (7.772 g, 71.87%). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.38(dd, 4H), 7.92–7.29 (m, 12H), 2.73 (s, 6H); ^{31}P NMR (122 Hz, $CDCl_3$, δ): 23.51; ^{13}C NMR (75.4 Hz, $CDCl_3$, δ): 197.1 (C=O), 142.2, 136.2, 135.4 (d, 10.5 Hz), 134.7 (d, 9.7 Hz), 131.2 (d, 13.5 Hz), 130.3 (d, 12.7 Hz), 122.8 (d, 88.5 Hz), 117.1 (d, 88.5 Hz), 27.4 ppm. Anal. calcd for $C_{28}H_{24}PO_2Br$: C 66.81; H 4.81; found: C 65.56; H 5.00%.

#### Synthesis of P1

The cyclotrimerization procedures followed the method described previously.[30] In a typical reaction, **M1** (0.491 g, 0.975 mmol) and *p*-toluenesulfonic acid monohydrate (PTSA, 0.928 g, 4.88 mmol) were mixed in a glass vial and heated to 120 °C for 24 h under N_2. Soxhlet extraction with ethanol yielded red-brown chunks (0.430 g, 93.8%); anal. Calcd for repeat unit formula $C_{78}H_{57}P_3Br_3$: C 70.60; H 4.33; found: C 71.05; H 5.07%. The reaction can also be carried out in a stainless steel reaction vessel to yield a reddish-brown film. Films prepared in this way were soaked in ethanol for 3 h to remove excess PTSA prior to drying, IR spectroscopic analysis, TEM and AFM imaging of films.

For physisorption analysis of **P1**, the solid was ground in a ball mill for 25 min to yield a yellow powder. The IR spectrum of **P1** in powder form was taken to ensure no side reaction happen (Fig. S5).

Characterization

All the NMR spectra were collected on a JOEL ECX-300 MHz spectrometer operating at 300, 121.4 and 75.4 MHz for ^1H, ^{31}P, and ^{13}C, respectively. Thermogravimetric analysis (TGA) was performed on TA Instruments Q60 TGA from 25 °C to 800 °C with a heating rate of 5 °C min^{-1}. Powder X-ray diffraction was measured on an Ultima IV. Fourier transformed infrared spectra were recorded on Shimadzu IRAffinity-1S at
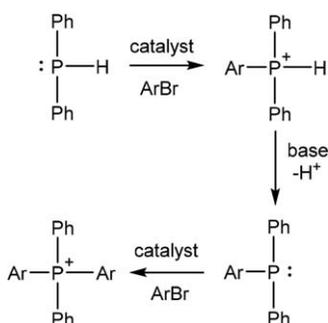
SCHEME 2 P–C coupling route to $[Ar_2PPh_2]^+$ salts from $HPPh_2$.

400–4000 cm^{-1} at room temperature. Nitrogen and CO_2 sorption measurements were collected on a Quantachrome ASIQwin^{TM} at 77 K and 273 K, respectively. The samples were degassed at 80 °C for 7 h before measurements. BET surface areas are determined over a P/P_0 range. Scanning electron microscopy (SEM) was performed on a Hitachi SU-6600 at 20 KV. A Hitachi H9500 transmission electron microscope, operating at a voltage of 300 KV, was employed for direct observation of film of **P1**. Film sample were first mixed with LR white embedding resin (catalyzed) and dried at 60 °C overnight. The sample was then cut to yield 80 nm thick slices. Sample slides were dried in air and placed on a 200 carbon formvar copper TEM grid for observation. Atomic force microscopy (AFM) images were collected using an AIST-NT SmartSPM in non-contact mode with HQ:NSC14/AL BS cantilevers from Mikro-Masch with spring constant of about 5.0 N/m. The **P1** in film was used directly without any treatment. AFM images were processed with AIST-NT SPM Control Software.

For base stability measurement, solids (~20 mg) were soaked in ~5 mL of 6 M NaOH(aq) at room temperature or at 60 °C for a 24 h period. Then the solids were soaked in DI water for another 24 h to remove excess hydroxide ions. The sample was dried in a vacuum oven at 40 °C for at least 24 h prior to analysis by FT-IR spectroscopy.

To assess water uptake, a powder sample was soaked in DI water at room temperature for 24 h and then weighted (W_w) after the water on the surface was removed. The wet solid was dried in a vacuum oven until the weight remains constant (W_d) to confirm the reversibility of the process. The formula to calculate water absorption was: water absorption = $(W_w - W_d)/W_d \times 100\%$.

RESULTS AND DISCUSSION

Design of Synthesis

The proposed synthetic route for **M1** was inspired by the Ni-catalyzed P–C coupling route described by Cristau's group (Scheme 2).[24,31] This method involved using an excess (~5 equiv) of tolylbromide as solvent/reactant and heating at 200 °C for at least 24 h with ~70% yield. To decrease the amount of wasted aryl halide, shorten the reaction time, and improve the yield, we modified the procedure to include diisopropylamine as a base to facilitate the requisite
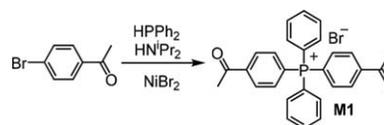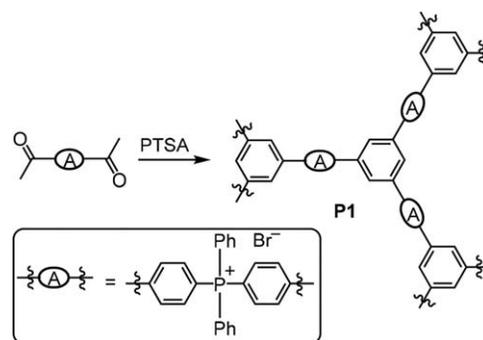

SCHEME 3 Synthetic route to prepare **M1**.

deprotonation steps.[24] Under these conditions, we found that the reaction was quantitative in ethylene glycol solvent after 15 h at 180 °C under N_2. Upon workup, **M1** was isolated as a highly hygroscopic yellow powder (Scheme 3).

To confirm the stability of a phosphonium species to the reaction conditions, commercial tetraphenylphosphonium bromide was first heated with PTSA under conditions identical to those used for the proposed cyclotrimerization. No degradation of the tetraphenylphosphonium salt was observed under these conditions, as probed by NMR spectra.

Cyclotrimerization of **M1** was then carried out in a glass vial with 5 equiv of p-toluene sulfonic acid (PTSA) at 120 °C under N_2 (Scheme 4). The mixture melted around 100 °C, initially yielding a viscous yellow liquid. After 24 h of heating, the mixture had solidified, resulting in a dark brown monolith that holds the shape of the glass reaction vessel. When a shallow stainless steel mold was used, the mixture formed a very smooth film (as determined by AFM, vide infra). The cyclotrimerization of **M1** proved to be a facile route to synthesize tetraarylphosphonium material to form smooth films or a variety of shapes based on the reaction vessel employed.

Removal of excess PTSA from as-prepared **P1** was affected either by soaking the film in ethanol or by Soxhlet extraction with ethanol. The molecular composition of **P1** (in both powder and film state) was determined by IR spectroscopy (Fig. 1). Solution NMR analysis was not possible due to the characteristic insolubility of network solids. By comparing the IR spectra of monomer **M1**, p-toluenesulfonic acid and **P1** in powder and film (Fig. 1), it is clear that the carbonyl groups (C=O stretch at 1680 cm^{-1})[32] have been completely consumed (within instrument detection limit) with concomitant emergence of the C=C stretch at 1600 cm^{-1} attributable to the 1,3,5-trisubstituted benzene rings in **P1**. A very weak

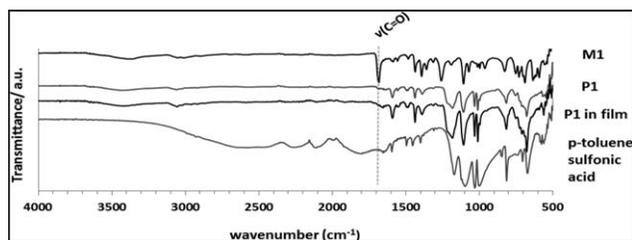**SCHEME 4** Synthetic route to prepare **P1**. PTSA = p-toluenesulfonic acid.

FIGURE 1 IR spectra of **M1**, **P1** (powder), **P1** (film) and *p*-toluene sulfonic acid.

band at 890 cm^{-1}, attributable to out-of-plane bending vibrations of 1,3,5-trisubstituted benzene rings,[25] is also present in the FT-IR spectrum of **P1** but not in the spectrum of **M1**. The characteristic H-bonding-broadened absorption band in the IR spectrum of PTSA is absent in **P1** (powder and film), thus confirming its success removal in the workup. The conversion from **M1** to **P1** was also confirmed by the close agreement between theoretical and experimental composition of **P1** as determined by elemental microanalysis. The cross-linking degree in **P1** was calculated according to the reported procedure[25] based on the integration ratio of the absorbance band for aromatic C—H (3000–3150 cm^{-1}) and aliphatic C—H stretches (2750–2975 cm^{-1}). The degree of cross-linking for **P1** calculated by this procedure is 67%, which is notably higher than the value of 49% reported previously for a neutral analog. The efficient conversion of **M1** to **P1** is a significant improvement over the extents of reaction observed in the preparation of many neutral materials prepared by analogous methods. The X-ray powder diffraction analysis indicates that the material so-formed in amorphous (Fig. S4).

Thermal and Chemical Stability

On the basis of our prior work with linear tetraarylphosphonium polymers,[24,33] we expected **P1** to have good thermal stability. TGA was thus applied to probe the thermal stability of **P1**. The 5% decomposition temperatures ($T_{d,5\%}$) for **P1** are 379 °C and 370 °C in air and N$_2$, respectively (Fig. 2). This value is comparable with the other polymer networks, for example, the diamond-like framework from the tetrahedral-vertex solid **R4** (Scheme 1B).[4] Compared with
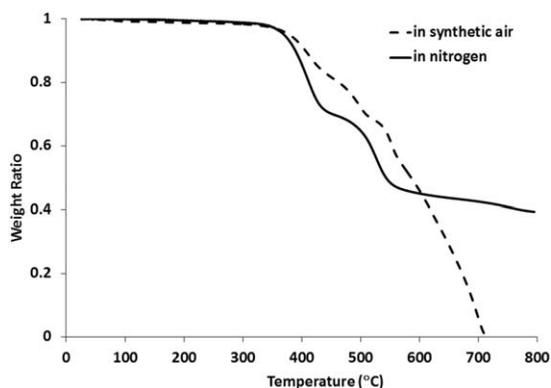

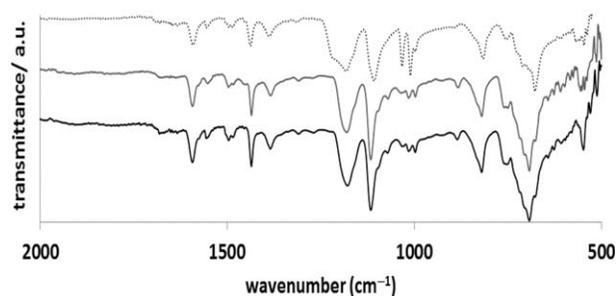**FIGURE 2** TGA curves of **P1** under N$_2$ (solid line) and synthetic air (dashed line).

FIGURE 3 IR spectra of **P1** (top, dashed line) and **P1** after soak in 6 M NaOH for 24h at room temperature (middle, gray line) and 60 °C (bottom, black line).

neutral polymers prepared by same method, **P1** shows better thermal stability which is attributable at least in part to the absence of unreacted acetyl groups. Under N$_2$, **P1** has a char yield of about 40%, which is higher than most organic polymers but typical of other high-aromatic-content materials. In air the weight loss is essentially complete at ~710 °C, comparable with what was observed for other polymers synthesized via cyclotrimerization.

Tetraarylphosphonium polyelectrolytes are of particular interest compared with alkylphosphonium analogs due to their generally improved alkaline stability.[22,24] To assess the extent to which **P1** withstands alkaline exposure, films of the material were soaked in 6 M NaOH solution at room temperature or 60 °C for 24 h. The structure of **P1** after base treatment was determined by IR spectra (Fig. 3). A comparison of the spectra before and after base treatment reveals that they are almost identical other than the change in peaks at ~1000 to 1050 cm^{-1} attributable to the expected exchange of bromide to hydroxide counteranion in **P1**,[34] without loss of the phosphonium network structure. The good chemical stability indicates that the highly cross-linked network in **P1** could prevent the attack from hydroxide ion.

Film Morphology and Physisorption

As-synthesized films of **P1** were examined by atomic force microscopy (AFM), revealing a very smooth surface with root mean squared roughness (R_{rms}) of 3 nm (AFM images are provided in Figure S6A,B of the Supporting Information). The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images (Figs. S6C and S7 of the Supporting Information) showed that **P1** has a layered structures similar to those of a polymer previously synthesized via cyclotrimerization,[30] but revealed no other features of note.

The surface area measurement was carried out by nitrogen physisorption at 77 K (Fig. 4). The isotherm shape is typical for type-II isotherms according to the IUPAC classification, indicating a non-porous material.[35] The specific surface area and total pore volume based on BET are 9.021 m^2/g and 0.014 cm^3/g, respectively. This value was comparable with some charged polymer made from ionic liquids via
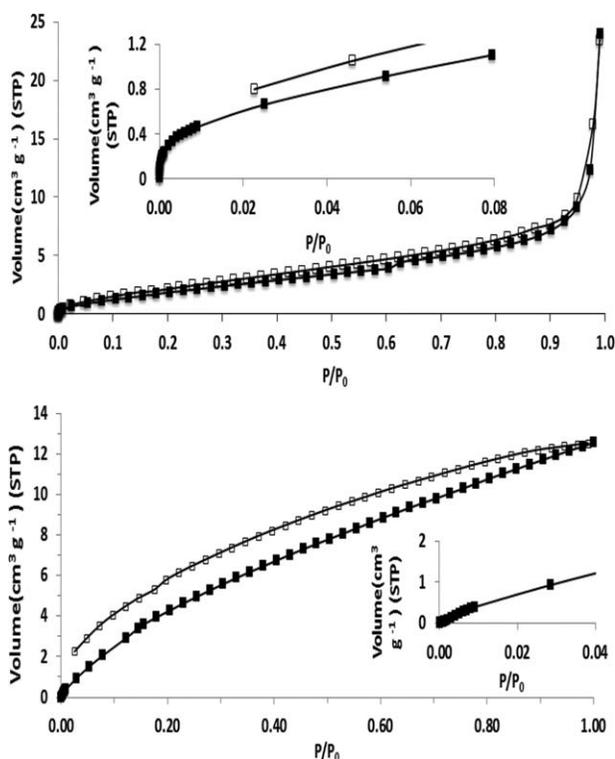
FIGURE 4 Nitrogen sorption isotherms at 77 K (top) and CO_2 sorption isotherms at 273 K (bottom) of **P1**. Adsorption points are presented by filled squares and desorption by empty squares.

cyclotrimerization as well as other organic frameworks.[28] Polymers tend to form non-porous solids when flexible chains allow for space-efficient packing.[36] Another possible reason for the small specific surface area of **P1** is due to the better solubility of **M1** in *p*-toluene sulfonic acid, which leads to less macrophase separation and formation of a more closely layered structure during synthesis.[36] A similar situation was observed by the Kaskel group when they used different monomers bearing diacetyl group to synthesize polymers. They found that monomers bearing amino groups tend to have nonporous structure because the amino groups were protonated to form ammonium moieties during synthesis, leading to a better solubility in molten *p*-toluenesulfonic acid through ion pair formation.[10] The phosphonium moieties in a growing sample of **P1** similarly improve its solubility in the highly polar PTSA versus neutral organic monomers. This may also explain the improved extent of reaction in forming **P1** compared with that observed for materials prepared from less soluble neutral analogs.

The ionic nature of **P1** could potentially be exploited for selective interaction with polar molecules. To asses this possibility, we examined the ability of **P1** to adsorb CO_2. The sorption isotherms of CO_2 at 273 K indicate a type-II material. During the whole process, the volume increases gradually, which indicates a stable physisorption as pressure increases. The specific surface area measured by BET is 27.913 m^2/g, which is larger than the result yield by N_2. This is as

expected, because CO_2 is known as a surface sensitive gas and the isotherm shape/surface area measured for CO_2 reveals a stronger interaction between **P1** and CO_2. This observation is also consistent with the widespread use of phosphonium salts as CO_2 capture/catalysis reagents.[6]

Water is another polar molecule that might be expected to be taken up by **P1**. Due to the non-porous structure of **P1** revealed by N_2 sorption, the water uptake is only 10.63%. This number is comparable with the values reported by Kaskel ($12 \pm 3\%$), which indicates weak interaction with water.[10]

CONCLUSIONS

A versatile route for phosphonium-modified framework synthesis via cyclotrimerization was demonstrated. The polymer shows good alkaline and thermal stability as well as affinity for CO_2. These properties suggest potential applications in gas separation, catalysis and alkaline fuel cells.

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